Investigation fo Thermoelectricity for Metallic and Silicate Minerals

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Abstract

For subsidiary investigation of the mechanism of electric conduction, the thermoelectricity of galena, pyrite and magnetite of metallic minerals and quartz and perthite of silicate minerals were measured in the temperature range from room temperature to about 600°C. Galena, pyrite and magnetite showed the behaviour corresponding to metal excess semiconductor. Perthite showed the conduction predominated by the impurity electron in the temperature region of this experiment. Quartz showed a similar behaviour to perthite at lower temperature, but, in the temperature region above 450°C, presented positive thermo-e.m.f. conditioned by "positive hole", and a remarkable anomalous change was observed in the vicinity of the well-known inversion point.

1 Introduction

In general, the electrical conductivity of rocks increases with temperature in a similar way to that of ionic- and semi-conductor. The author reported in the previous paper [1] the results of investigation for the electrical conductivity of a few silicate minerals. According to the results, the electrical conductivities for these silicate minerals indicated, in most cases, three marked process in the range of temperature up to about 600°C, from 600°C to about 1000°C and above 1000°C. Recently, it was reported that the similar three processes was observed by H. HUGHES in cases of the ferromagnesium silicates such as olivine and pyroxene mineral groups [2]. Of these three process, the ones in higher temperatures above 600°C had been examined in detail and known they are an electronic semiconduction or an ionic conduction. On the other hand, for the process in lower temperatures below 600°C, it may be necessary to study in more detail what mechanism predominates in the process and what kind of charged particles play the main role in conduction. For these problems, the measurement of the Hall effect or the thermoelectricity as well as the electrical conductivity has been carried out in the previous studies. The thermoelectricity was measured in this experimet.

As well-known, the change of the thermo-e.m.f., V, of a semiconductor is expressed as follows [3] [4] ;

$$\frac{dV}{dT} = F(T) - \frac{\Delta E}{2eT}, \qquad (1)$$

where ΔE is activation energy and the term $F(T)$ is, in general, a function secondarily and scarcely related to temperature. The convention adopted for the sign of the thermo-e.m.f. is that the flow of electrons from semiconductor to metal at the hot junction is denoted as positive. This corresponds to the "positive hole" conduction within the semiconductor which is brought about by a stoichiometric excess of non-metal, while a negative sign of the thermo-e.m.f. corresponds to electron conduction conditioned by a stoichiometric metal excess.

From this point of view, it is possible to estimate the sort of charged carrier at any temperature for each mineral which is considered as semiconductor. Comparing the results of metallic minerals with those of silicate minerals, it may be decided whether the conduction mechanism in both cases are similar or not.

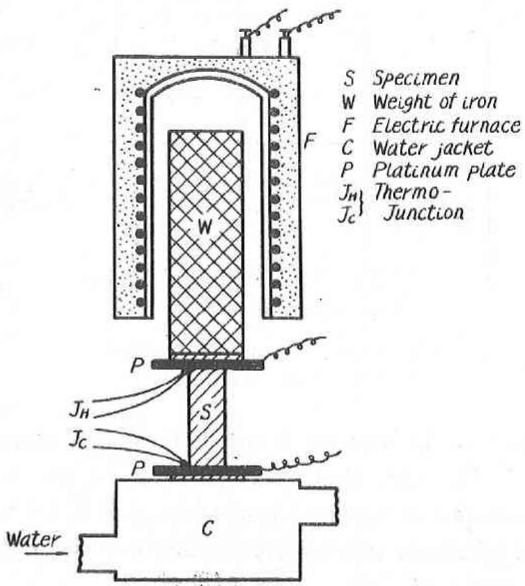

Fig. 1 Main Parts of experimental arrangement

2 Experimental Method

The samples used for measurement were pyrite, galena, magnetite, quartz and perthite. The places of production of these samples were as follows;

pyrite	Daira mine, Akita Prefecture, Japan
galena	Daira mine, Akita Prefecture, Japan
magnetite	Kamaishi, Iwate Prefecture, Japan
quartz	Brazil
perthite	Suisyoyama, Fukushima Prefecture, Japan.

The columnar specimen was mounted on the supporter as illustrated in Figure 1. Two ends of the specimen were pressed against platinum plates to form the hot and cold junctions. In this case, an iron weight was placed on the specimen in order to ensure firm connection between the specimen and platinum plates. A water jacket functioning simultaneously as the supporter at the lower end of the specimen and a small electric furnace surrounding the upper end produced a temperature difference between the two ends of the specimen. In cases of metallic minerals, the thermo-e.m.f. was measured by means of a potentiometer, using a sensitive galvanometer as indicator at higher temperatures, and a quadrant electrometer at lower temperatures. For silicate minerals, only the quadrant electrometer was used. The temperatures

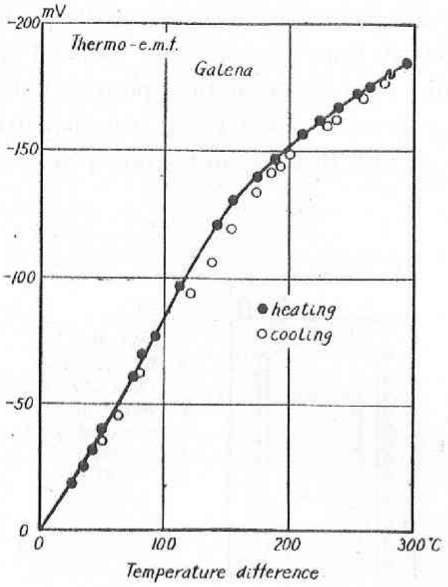

Fig. 2 Thermo-e.m.f. and temperature difference for galena

of the two ends were measured with the aid of chromel-alumel thermo-junctions.

3 Results of Experiment

Experiments were performed on two or three specimens prepared from a sample. However the results for each specimen of a sample were very similar. The variation of e.m.f. with temperature difference is shown in Figures 2–7. The temperature difference of abscissa can be considered as the temperature at the hot junction, because the value of thermo-e.m.f. is reduced to that corresponding to the temperature of cold junction being 0°C. In Figures 8 and 9, dV/dT is plotted against $1/T$. The measurement was carried out in air in all cases. However, this operation does not cause any essential influence to the results obtained. As seen in Figures 2 and 4, the curve corresponding to the cooling process is well coincide with that corresponding to the heating one. Therefore, the effect of oxidation of specimen is considered to be trivial. In this paper, the effect of oxidation of specimen will be not discussed in more detail, for it is not the purpose of this experiment.

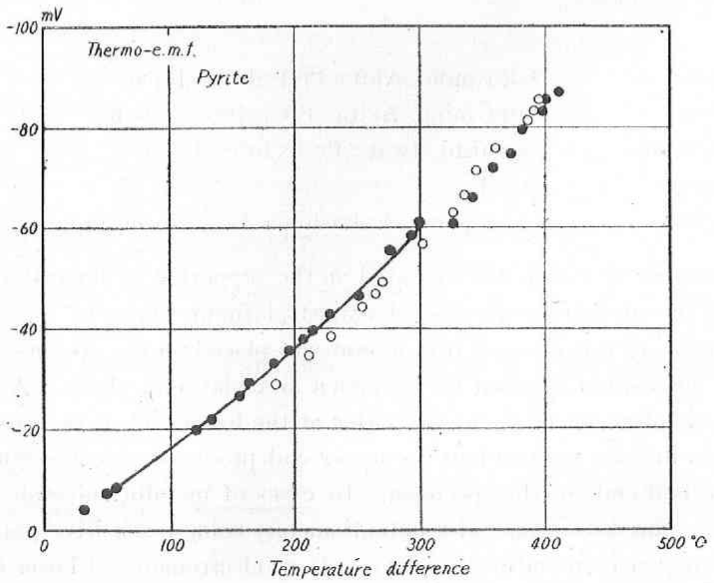

Fig. 3 Thermo-e.m.f. and temperature difference for pyrite

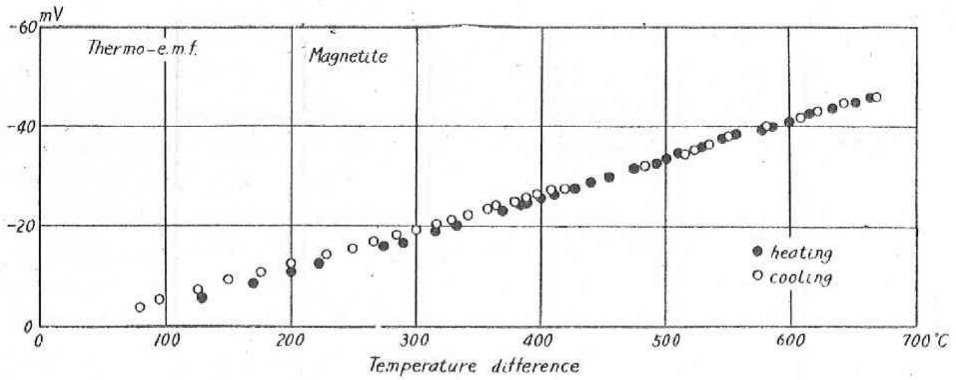

Fig. 4 Thermo-e.m.f. and temperature differecen for magnetite

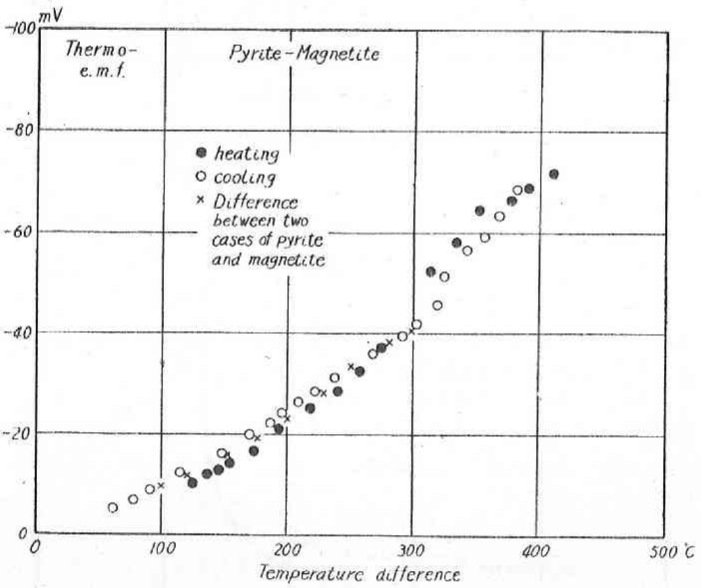

Fig. 5 Thermo-e.m.f. and temperature difference for pyrite-magnetite coupled system

It is understood, at first, from the results in the metallic minerals that galena shows the most remarkable thermo-e.m.f., followed by pyrite, and magnetite is the smallest. For pyrite as well as galena, the e.m.f. varied discontinuously at about 300°C, and it changed reversibly in both cases in heating and in cooling when the processes falls on the range of temperature below about 300°C. However, the curve in cooling from the temperature above about 300°C showed some departures from that in heating. The departure seems to be the evaporation of sulpher composing the minerals, in other words, it results from the changes in chemical composition and crystal structure.

On the other hand, as seen in Figure 4, magnetite showes reversible change over all temperature ranges in the experiment. The discontinuous change of thremo-e.m.f.

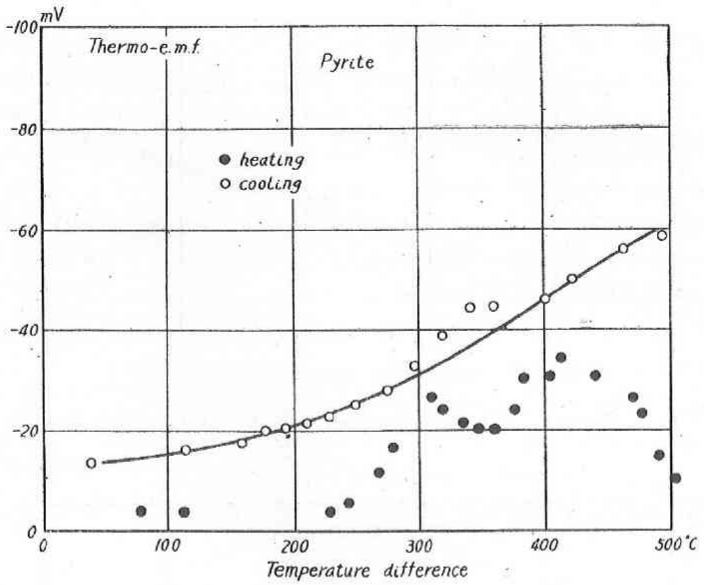

Fig. 6 Thermo-e.m.f. and temperature difference for perthite

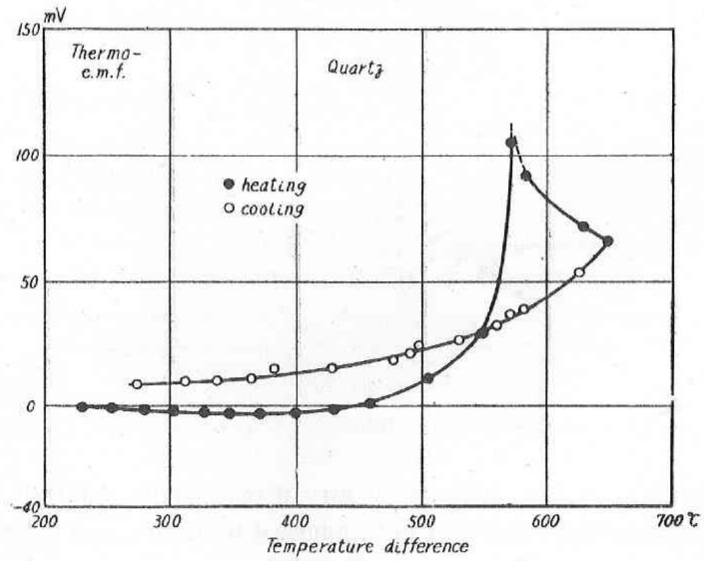

Fig. 7 Thermo-e.m.f. and temperature difference for quartz

of magnetite is found at about 575°C, corresponding to the well-known Curie point of magnetite. The values of dV/dT at the temperatures higher than 575°C decrease with increasing in temperature. From this fact, it may be considered that the thermo-e.m.f. of a ferromagnetic substance as magnetite varies discontinuously at the Curie point.

Furthermore, the coupled system of two minerals were examined. As an example, the result for magnetite-pyrite system is illustrated in Figure 5. Comparing the curve

of this coupled system (Fig. 5) with those of magnetite and pyrite (Fig. 4 and 3), it is directly understood that the value of e.m.f. at any temperature difference of the coupled system is coincident with the difference between the two values of magnetite and pyrite at the same temperature difference. This fact gives us a suggestion that the e.m.f. of an actually existent rock composed of such metallic minerals in the present case are due to a similar mechanism stated above.

As for quartz and perthite of silicate minerals, it is found at first that they show remarkable anomalous changes in thermo-e.m.f.. In case of perthite, the sign of e.m.f. is negative and the same to that of the above mentioned minerals, but some anomalous changes in heating process are represented, while no abnormal variation in the cooling process is found. As for quartz, on the contrary to other samples, the e.m.f. has positive sign except the lower temperature region in the heating process,

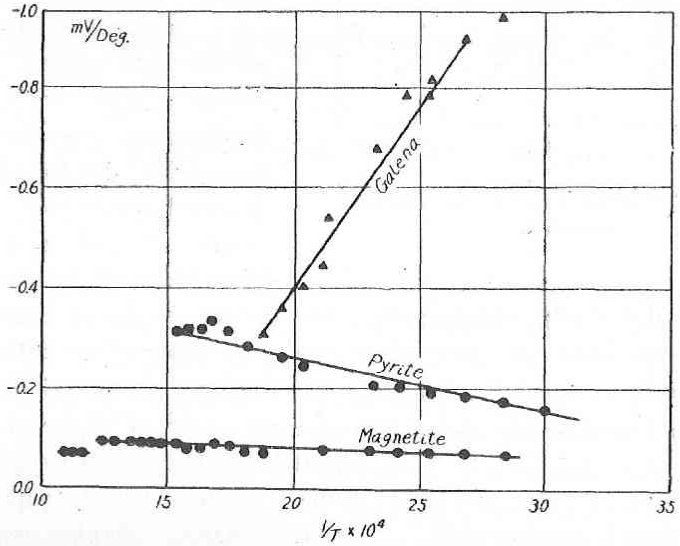

Fig. 8 dV/dT and $1/T$ curves for metallic minerals

and it shows an abrupt change in the vicinity of its inversion temperature. In the cooling process of quartz, the e.m.f. varied smoothly as seen in Figure 7.

4 Discussion

As stated above, most of these samples except quartz, showed negative sign of e.m.f.. Consequently, if the theory of semiconductor is applicable for these minerals, it is expected that the electrical conduction within the specimen is mainly contributed by electron. However, it is premature to conclude from these results that the conduction is electronic, because in general the electronic conduction and the "positive hole" conduction occur simultaneously. When these two conductions occur in a specimen, it may be reasonably accepted that the electronic conduction is more predominant statistically than the positive hole conduction within the mineral.

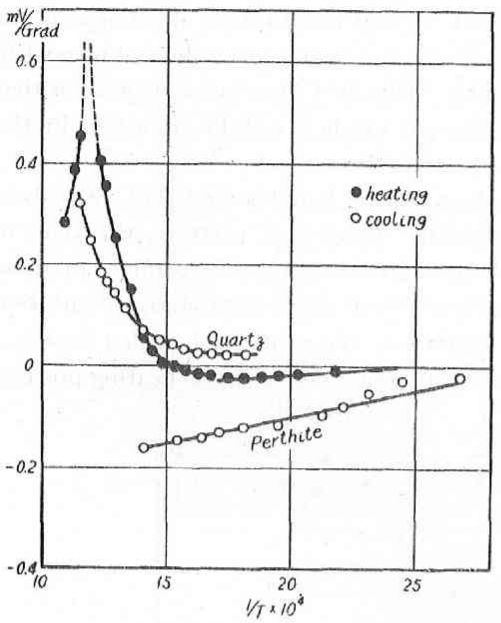

Fig. 9 dV/dT and $1/T$ curves for silicate minerals

Moreover, for metallic minerals, a linear relation exists between dV/dT and $1/T$ as given in the following formula;

$$dV/dT = -a + b/T, \qquad (2)$$

where b corresponds to $\Delta E/2e$ in equation (1). Namely, the same formula as expected from the theory of semiconductor come into existence. The values of ΔE for respective samples are shown in table 1.

Against the minerals mentioned above, the character of negative e.m.f. in cases of silicate minerals, perthite and quartz, seems to be caused by some different origin, for the processes in these cases are irreversible. On the other hand, the electrical conductivity of the same samples of quartz and perthite have been observed by the auther (1). As compared the results obtained by the present experiment with that in the conductivity experiment, an irreversible change is observed in both cases at the same temperature range. Meanwhile, any structure change of these minerals have not been known within such a temperature region as observed abnormality. Therefore, we cannot attribute the abnormal changes of these silicate minerals, to their structure change. Besides, according to the results from the experimental data for electrical conductivity at higher temperatures [1] and to the mineralogical and other theoretical considerations, the phenomena cannot be explained to be proper to the essential structure of gitter. Because, if these phenomena are related to the gitter structure, they should be reversible changes and, moreover, the activation energy should be far larger than present one. Consequently, by the opinion of the author, the phenomena are caused by the inclusion in the specimen, that is, the negative thermo-e.m.f. is due to the conduction conditioned by the impurity electron within the specimen of perthite or quartz.

Table 1.

Samples	E (eV)
galena	3.0
pyrite	1.0
magnetite	0.03
perthite	0.3
quartz	0.2*

* The value corresponds to that in heating process at lower temperatures.

The remarkable anomalous change for quartz in the vicinity of 570°C is regarded

as a phenomenon caused by the well-known structure change from α-quartz to β-quartz. The thermo-e.m.f. of quartz is positive in the vicinity of its transition point and in the cooling process. The positive sign of the e.m.f. indicates that the positive hole conduction predominates in the specimen.

The relations between dE/dT and $1/T$ for perthite and quartz are shown in Figure 9, where the values for perthite are adopted from those corresponding to the cooling process. This is because the change in the heating process of perthite was so irregular that the reasonable values were not obtained. In the case of quartz, as seen in the Figure 9, the linear relation between dV/dT and $1/T$ does not exist in most temperature ranges except in lower temperatures in the heating process. The values of activation energy ΔE for perthite and quartz are shown in Table 1, where the value for perthite is adopted such one corresponding to the cooling process and for quartz the corresponding one to heating process in lower temperatures below 400°C.

Although the activation energy obtained from the data of electrical conductivity do not coinside exactly with the present one, their order of magnitude of the two are the same when the average of many experimental data are taken into consideration. In addition, the values of activation energy for perthite and qurtz may be considered to be in the order of 0.2–0.3 eV in lower temperature range where the conductions are predominated by the impurity electron within these specimens

5 Conclusion

In the temperature range from room temperature to about 300°C, the thermoelectricity of galena and pyrite are negative and the electronic conduction predominates within these minerals. The activation energy of galena and pyrite are estimated to be 3.0 and 1.0 eV respectively. Magnetite shows also negative thermo-e.m.f. conditioned by the electronic conduction. The thermo-e.m.f. of magnetite changes discontinuously at the Curie point and the absolute value of dE/dT decreases with increasing temperature above the point. The activation energy in lower temperatures is 0.03 eV.

The conduction of silicate minerals, i.e., perthite and quartz, are mainly due to impurity electron in lower temperatures, but, for quartz, the thermo-e.m.f. becomes positive in the vicinity of the inversion point. This showes that the conduction in lower temperatures is accompanied by the positive hole. The activation energy of perthite and quartz in lower temperatures are 0.3 and 0.2 in their orders of magnitude.

In conclusion, the auther thanks Prof. Y. Kato for his supervision and encouragements on this study.

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